

**SAFE OPERATING PROCEDURE**

**FOR**

**THE USE OF HYDROFLUORIC ACID**

**AND SOLUBLE FLUORIDES**

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*Curiosity may have killed the cat, but curiosity about your work may save your life.*

## 1 Introduction

Hydrofluoric acid or HF is a virulent neurotoxin, a muscle inhibitor, and causes bone disintegration, all in addition to its corrosive and tissue destroying effects as an acid. HF is readily absorbed through the skin, mucus membranes, and the lungs. Untreated or incorrectly treated exposure to HF is usually life-changing. Rinsing an exposed area is inadequate on its own because the substance is so rapidly absorbed that the internal consequences need to be dealt with at once.

## 2 Use of Hydrofluoric Acid

### 2.1 Approved users

The use of HF is governed by the local rules contained in this document. HF and related substances may only be handled by Approved Users in a work station or fume cupboard designated specifically for the purpose. To become an Approved User it is necessary to pass the University HF safety course on Moodle and demonstrate practical competence to the local laboratory supervisor. A detailed knowledge of this document will be expected.

- Under no circumstances will undergraduates be allowed to work with HF.
- The devolution of responsibility for working with HF to an untrained person is a disciplinary offence.
- Approved Users do NOT have a mandate to give training.

### 2.2 The Operator – Observer (OO) Principle

The University safety procedure is based on the **Operator-Observer** (OO) principle. An individual working with HF (the Operator) will be accompanied at all times by an Observer. Both parties must be Approved Users of HF.

- The role of the operator is to perform the necessary process in accordance with these rules and any specific working procedure.
- The roles of the observer:
  - Provide immediate emergency first aid in the event of an accident where this is consistent with their own personal safety;
  - Summon more general first aid;
  - Ensure that the emergency services are called;
  - Ensure that any other necessary action is taken (this may include evacuation of the laboratory or the building)
  - If necessary, to provide the information on the Emergency Card to medical staff involved in treating the exposed person
- The OO principle applies to HF at all times, meaning that ONLY approved users may transport containers of HF around the building and they must be accompanied by an observer.

## 3 Working environment

### 3.1 The Chemicals

Open HF containing vessels must not be taken outside a workstation or left unattended except in an emergency. All chemicals which are left unattended, or which are to be transported, must be in closed containers made from suitably resistant materials and have secure lids. Such containers must

be indelibly labelled with the name of the chemical they contain and its concentration. Chemicals in sealed containers must be returned to an appropriate store and not left in the workstation.

### 3.2 The HF Workstation

The working surfaces in the work station will be kept clear and uncluttered using the minimum amount of space for chemical containers and equipment. The work station will not be used to store chemicals. The safety equipment listed in the table below will be available immediately adjacent to any HF workstation. The operator and observer should ensure that these are in place before commencing work.

What	Minimum quantity	Comment
Calcium gluconate gel	2 x 500 g tubs	Small tubes are not acceptable. Topical application to exposed skin.
Hexafluorine ® solution	Wall mounted grab pack	Effective chelation and barrier for HF in eyes or on skin, and as a mouthwash
Milk of magnesia	1 x 200 mL bottle	Essential if HF is swallowed (MgO chelates fluorine ions)
Snug fit disposable gloves (surgical glove style)	S, M, L and XL to be supplied 1 pack 100 in use 1 pack 100 reserve	Nitrile or neoprene, must be seamless
Spill-X-A powder	1 x 22.7 kg plastic pail	High proportion of MgO, suitable for spills outside workstations
Spill-X-A powder	1 x 1.1 kg container	For small spills
3M 9906 Nuisance masks	3	To be worn where spills occur outside the workstation
Emergency Card providing contact details and information for medical staff about the chemical involved.		

A suitable chemically resistant dosing pump attached to the HF bottle should be provided to ensure that the chemical does not have to be poured between vessels.

Work with the sash in the lowest practical position, and never raise the sash above the maximum level marked when the work station contains any HF. Never put your head inside the workstation when attempting to clean up spills.

## 4 Transporting HF

It is inevitable that HF will need be transported through the building between stores and the laboratory where it is to be used. The following procedure must be followed:

- When transporting HF through the building, plan the route in advance and avoid times when there is likely to be high volumes of pedestrian traffic;
- When transporting HF through the building, place the HF bottle inside a securely lidded secondary containment vessel, which is resistant to HF;
- The OO pair will carry HF resistant disposable gloves, HF nuisance masks and a supply of Spill-XA to be used in the event of an emergency.
- Do not use the lifts;

## 5 The effects of HF exposure

Fluorine ions react with calcium and magnesium ions in solution to form insoluble precipitates. This reduces the levels of calcium and magnesium in the blood stream causing hypocalcaemia and hypomagnesaemia. The fluorine ions combine with calcium in bones, The effects of exposure may take a significant time to produce symptoms, up to 24 hours for a limited exposure to a low concentration.

Depending on the level of exposure the symptoms may include

- severe tissue damage resulting in mortification of bones, muscles, skin.
- extreme pain, a dull ache, lack of sensation
- paralysis
- shock
- confusion
- massive organ failure
- unconsciousness
- death

## 6 First aid and subsequent steps

### 6.1 Introduction

IN ALL CASES, SUSPECTED EXPOSURE SHALL BE TREATED AS EXPOSURE.

**The Observer is responsible for giving immediate HF-specific first aid.**

At the earliest opportunity phone 22222 (or get someone else to do this) and arrange for an ambulance. You may also summon help from Departmental First Aiders.

In all cases of exposure, medical and paramedical staff must be made aware that the patient has been exposed to hydrogen fluoride (see Emergency Card) and that the remedial treatment differs from that for other acids.

In all cases, those administering emergency first aid must take actions to minimise further exposure, particularly for themselves and the victim, and to ensure the safety of others working in the vicinity.

### 6.2 If the victim has suffered skin contact with HF:

- Don the appropriate protective equipment (see section 7, Personal Protective Equipment).
- Remove all affected clothing as rapidly as possible, but with as little further contact to the affected individual as possible. Lay this aside safely (e.g. in a bucket of water in the work station for later safe disposal or double bagged in polyethylene bags). DO NOT RINSE THROUGH CLOTHING – this will spread the problem around.
- Rinse/slurp off the affected area for 3-5 minutes with Hexafluorine® solution. Continue with copious quantities of fresh water in a jet or from a soft dispersal nozzle.
- Immediately apply liberal quantities of calcium gluconate gel to the affected region. Keep on rubbing this in both locally and around the affected area.
- The victim MUST be removed to hospital, and calcium gluconate treatment MUST be continued in the ambulance (see Emergency Card).

### 6.3 If the victim has inhaled or ingested HF:

These steps may be required in addition to those in 6.2 above.

Don the appropriate protective equipment (see section 7, Personal Protective Equipment).

- If the victim has HF splashed in or inhaled through the nose, irrigate with Hexafluorine® solution.
- If the victim has swallowed HF, wash the mouth out with Hexafluorine® solution;
- Do not give large quantities to drink. Do not induce vomiting;
- It may be useful to give about half a cup of water, milk, or anti-acid (e.g. Milk of Magnesia in water);
- If the victim vomits spontaneously, assist them with physical support. The vomit should be treated as an HF hazard;
- The victim must be removed to hospital as soon as possible, even if there are no visible signs of exposure.

### 6.4 If the victim has suffered eye contact with hydrofluoric acid

Don the appropriate protective equipment (see section 7, Personal Protective Equipment).

- Immediately treat with Hexafluorine® eyewash according to the instructions. Continue to rinse the affected eyes with copious quantities of fresh water from a soft dispersal nozzle, or using a non-saline eye wash.
- The victim must be removed to hospital as soon as possible, even if there are no visible signs of exposure.

## 7 Personal Protective Equipment (PPE)

Adequate PPE can reduce a potentially lethal event to a minor inconvenience.

### 7.1 Requirements for Operators and Observers

The minimum PPE for working with hydrofluoric acid or soluble fluorides inside an approved workstation is:

- Full face splash proof visor to EN166 1 B 3 or better;
- HF-resistant full length, long sleeved smock
- HF-resistant boots
- Two pairs of HF-resistant gloves (for example, Neoprene or MAPA Trionic E194, both to be worn) or long HF-resistant gloves (as above, elbow or shoulder length) with a pair of disposable gloves worn inside
- Disposable HF nuisance mask (for example 3M 9906)

An individual giving first aid will need at least:

- Disposable HF-resistant gloves (two pairs, both to be worn)
- Disposable HF nuisance mask as above.

Some or all of the following may also be necessary depending on the level and concentration of the exposure

- Full face splash proof visor to EN 166 1 B 3 or better



- HF-resistant full length, long sleeved smock
- HF-resistant boots.

## 7.2 Dress code

1. The sleeves of the smock must be outside the gloves and not tucked into them, unless the gloves are elbow length or more, to prevent liquid spilled on the smock from flowing into the gloves.
2. The bottom of the smock must have an overlap of at least 150 mm with the tops of the boots, and must be worn outside them to prevent liquid splashed on the smock from flowing into the boots.

## 7.3 Gloves

### GLOVES DO NOT MAKE YOU SAFE!

The most common cause of HF exposure is a pinhole in a glove, so pay special attention to these.

The information available from safety data sheets indicate that Neoprene [the Du Pont trade name for poly(chloroprene)] gloves offer the best resistance to HF.

- Gloves must be seamless
- Gloves only ever offer splash protection.
- NEVER immerse gloved fingers in HF
- ANY glove splashed with HF should be rinsed, removed and discarded (in that order).
- If you use outer gloves which are “non-disposable” they must be replaced as above if splashed, and in any case every six months.

## 7.4 Care and maintenance

Each HF authorised user will be supplied with and expected to maintain their own PPE (with the exception of disposable gloves which will be available at the work stations). PPE will not be shared between individuals. Suspect PPE should be immediately discarded as hazardous waste and replaced. The responsibility for checking the integrity of PPE rests with the individual using it. If in doubt, replace your PPE.

If HF is spilt on the PPE, the affected item must immediately be carefully rinsed or sluiced off, in the workstation or the emergency shower nearby. It may well be best to do this without removing the item. This counts as a procedure involving HF and is subject to all the rules herein. In particular, the process must not create an additional hazard for the PPE owner or others in the vicinity.

Items must be thoroughly clean and dry prior to storage.

# 8 Accidents and Emergencies other than personal exposure

## 8.1 Spills within the workstation

If it is safe and practical to do so, neutralize the HF in situ using calcium carbonate, calcium hydroxide or magnesium oxide. In any case flush the HF away with a large quantity of water (large means at least 100 times the volume of split material) taking care to ensure no splash back occurs out of the workstation. Continue to sluice and flush for an extended period of time to ensure that no HF remains on any surfaces or in the sump underneath the workstation.

## 8.2 Small spills outside the workstation (less than 100 mLs)

All unprotected personnel must leave the laboratory or the area at once.

- If not already wearing them, the Operator and Observer will don HF nuisance masks, gloves and face shields.
- The spill shall be contained and neutralized using the dry material from a Spill-X-A tub as follows:

1. Do not lean over the spill.
2. Using the Spill-X-A powder to make a dam around the spill.
3. Gently apply a large quantity of Spill-X-A on to the spill.
4. After 10 minutes collect and store the solid product for waste disposal.

Report the occurrence to the Health & Safety Office as an accident.

### 8.3 Large spills outside the workstation (more than 100 mLs)

DO NOT ATTEMPT TO DEAL WITH THE SPILL.

- Evacuate the laboratory taking the Hexafluorine and calcium gluconate supplies with you.
- Deal appropriately with personal exposure (see section 6, First Aid), donning PPE if not already worn;
- Sound the fire alarm and leave the building;
- Continue the treatment of an exposed person using Hexafluorine and calcium gluconate gel as required;
- You must contact a senior member of staff (Safety Officer, the Departmental Administrator, the Head of Department or any other senior member of staff) at the first opportunity after leaving the building and explain the circumstances. It is vital that the Security Services are made aware of the nature of the emergency before entering the building to prevent exposure to HF vapours.

Report the occurrence to the Health & Safety Office as an accident.

### 8.4 Power cuts

Power cuts are not uncommon. All laboratories approved for HF use must have emergency lighting. In the event of a power cut, the extraction on the workstation or fume cupboard will stop.

Cover any open sources of HF if it is safe and practical to do so. All personnel must leave the laboratory and the doors must be shut.

The laboratory must not be re-entered until one hour after the extraction has restarted or until tests with an HF detector show that it is safe to do so.

## 9 Safe disposal

### 9.1 General procedure

HF (aq.) above 50 % reacts violently and exothermally with water, and violently with glass and other silicon containing materials such as concrete. This will result in the emission of extremely toxic fumes of HF or SiF<sub>4</sub> (silicon tetrafluoride).

- Dilution, if required, should be gradual. Concentrated acid should be added to water.
- Glass or silica containers must be avoided at all stages.
- Except in the event of a spill, the procedure will take place inside a work station
- In the event of a small spill outside a work station, a breathing mask will be required (see section 6).

Calcium and magnesium fluorides have very low solubilities in water and solutions of these do not represent a significant hazard. The safe disposal of HF or soluble fluorides involves

- Do not add water to concentrated acid (> 20%).
- Slowly add a precipitating agent to the correct amount (note for large quantities of high strength solution this may take several hours or even days).
- Check that the reaction is complete, the solution should be pH neutral or slightly alkaline).



- For neutralization of solutions containing less than 10 g of anhydrous HF at any strength the residues may be flushed down the drain at a dilution with water of at least 100:1.
- Larger quantities must be placed in an authorized container, clearly labelled, and sent for chemical waste disposal.

## 10 Glossary

HF	Used within this document as a generic term for preparations containing hydrogen fluoride at any strength. The dangers of other soluble fluorides, e.g. sodium fluoride, are similar, and this document applies to all these, even where only HF is mentioned specifically. These substances are extremely toxic because they are a source of fluorine.
HF (aq.)	Used when referring specifically to the aqueous solution of HF (hydrofluoric acid)
Hypocalcaemia	Lack of calcium in blood and body fluid – a principal cause of death when fluorine gets into the body.
Hypomagnesaemia	Lack of magnesium in the blood and body fluids, also extremely dangerous.
Spill kit	A proprietary kit (Spill X-A) to be kept by each workstation for use in the event of a minor spill outside the workstation.
Workstation	A fume cupboard, wet bench or other facility designated specifically for the use of HF.

# EMERGENCY CARD

## Exposure to HF

Call Security Services on 22222 (internal) or 02476 522222 (if using mobile)

**Location** *Input this information dependent upon location of HF workstation*

**Request** Emergency first aid support and call an ambulance

### Information for Medical Personnel

The casualty has been in contact with one of the following substances and may be suffering from acute poisoning due to absorption, ingestion, inhalation or instillation.

Aqueous solution of hydrogen fluoride (hydrofluoric acid)

Hydrogen fluoride gas

Other soluble fluorides in solution or solid form

### **Please seek immediate advice from a toxicologist.**

Appropriate first aid treatment using calcium gluconate gel (skin exposure), Hexafluorine® (skin, eyes), Milk of Magnesia, or similar (ingestion) may already have been given. The casualty may already have been externally decontaminated. The accompanying person can give more information.

- Medical staff should take precautions to minimize risk to themselves should the casualty still be externally contaminated. This may include an HF nuisance mask. Two pairs of surgical gloves and eye protection should be worn when initially handling the patient. Gloves should be rinsed prior to removal to prevent inadvertent contact with the substance;
- Vomit should be treated as chemically hazardous as it may be contaminated with HF;
- The casualty may be, or become, hypocalcaemic and hypomagnesaemic;
- Symptoms such as paralysis, loss of sensation, shock, severe burning, confusion, unconsciousness may be apparent immediately, or may develop over several days, depending in the level of exposure.